SYNTHESIS, CHARACTERIZATION OF A NOVEL CONJUGATED STRUCTURAL OLIGOMER

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ABSTRACT

An octupolar star-shaped ladder–type oligomer composed of electron deriving from 1,3,5-triazine core end-capped by either an electron donating carbazole moiety(TA(TL)-Ph(3)-CBZ) have been designed and synthesized to investigate the structure–properties relationship of highly efficient multiphoton absorbing materials. The newly synthesized molecules were characterized by 1H NMR, 13C NMR and mass spectrometry. Linear optical properties of the oligomer were investigated by UV-vis and fluorescence spectrometries, as well as the nonlinear optical properties were characterized by two-photon excited fluorescence (2PEF) measurement.

Keywords: Oligomer, TA(TL)-Ph (3)-CBZ, MPA, diphenylamine, tert(p-phenylene).

INTRODUCTION

Multi-photon absorption was first theoretically predicted by Maria Goeppert-Mayer (1906-1972) in her doctoral thesis in 1931. In her hypothesis, it was proposed that simultaneous two-photon absorption may take place in the quantum theory of radiation [1]. The theory was not confirmed until the construction of the first laser in 1960s. Invention of laser allowed the verification of two-photon absorption which is a third order optical process required a strong coherent light via the detection of two-photon-excited fluorescence in a europium doped crystal [2].

Three decades after the invention of laser, investigation of two-photon absorption was enhanced by higher viability of sub-picosecond level pulsed laser and the two-photon fluorescence microscopy by Webb and co-workers. In 1990s, development of femtosecond lasing techniques provided more spaces for in-depth nonlinear optical studies which drawn greater attentions from either chemical or physical scientists [3-5].

![Figure 1](image)

**Figure 1.** Primary structural motifs of dipolar, quadrupolar and octupolar chromophores where A, D and bridge line represents π-acceptor(π-electron deficient), π-donor (π-electron rich) and polarizable π-bridge respectively.

On early 1990s, the focus on multi-photon studies shifted from purely spectroscopic interests to development new multi-photon absorption active compounds. Nowadays, numerous principle applications are viable upon the rapid development of multi-photon active compounds, such as, three-dimensional (3D) imaging [6], 3D optical data storage [7], laser up-conversion[8], 3D microfabrication [9]. Nonlinear optical transmission, photodynamic therapy. Further studies of multiphoton absorption exhibited by amyloid fibres which are responsible for diseases, such as Alzheimer’s and Parkinson’s may bring out more inspiration for the therapeutic treatment of these diseases [10].

Essentially, highly efficient multi-photon absorption active compounds composed of three principle components: strong π-donor, strong π-donor and connected by polarizable π-bridge. The molecules possess MPA properties are mainly categorized into three classes (Fig.1) which included: (i) dipolar: A-π-D; (ii) quadrupolar: A-π-A; D-π-D; A-π-D-π-A; D-A-π-D; (iii) octupolar: 3-branched, D-core with A, branch, A-core with D, branch. Multiphoton absorption activities can be commonly observed in these types of compounds that drawing our attention to investigate the structure-properties relationship by either tuning the structure of end capped terminal or the acceptor or donor core [11].

To determine the sensitivity of a 2PA molecular entity in a quantitative approach, 2PA cross-section (σ) is employed as a parameter which describes electronic eigenstates as well as transition behavior of a molecule. Thus, the pivotal factor is utilized to evaluate the performance of a 2PA active molecule. Basically, the greater the value of 2PA cross-section, the higher of the ability is in preceding the intramolecular charge transfer[12-14]. Reported by Wong et al, multi-photon absorption activities are more desirable for the (L)-Ph(n)-NPh (with the number of phenyl rings n, ranged from 3 to 7) with a longer distance of conjugation system showed generally increasing 2PA and 3PA cross-section value. The intramolecular charge transfer would be the main focus on the following experiment on clarifying conjugated system. The MPA activities as electric polarization plays an important role in adjusting the MPA activities (Fig.2).

![Figure 2](image)

**Figure 2.** Structure of MPA active organic molecule (L)-Ph(7)-NPh

Composed of strong π-Donor or strong π-Acceptor, the π-conjugated system normally has a large transition dipole moment and low excitation value which enhances the 2PA capacities as well as the 2PA cross section [15].

Contributed by many scientists and research groups, numerous Type II and some Type III MPA active compounds were successfully synthesized [16-19] and characterized in the past two decades as investigation of MPA structure-properties relationship. The π-bridges could be unsaturated aliphatic chains or aromatic ring which connected the acceptor(such as: triazine, triphenylamine) and donors (such as, nitrogen-containing heterocyclic aromatic groups).

Inspired by the previous successful work on synthesizing highly efficient MPA active oligomers by Wong et al, N(TL)-Ph(3)-CBZ and TA(TL)-Ph(3)-NPh have higher potential of further development [20, 21]. In order to continue to investigate the properties of these oligomers, some derivatives can be made to figure out the MPA active oligomers.

Synthesizing weak-D, D-Core oligomers for the investigation on the relation between structural modifications and its MPA property will be a new trail.

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Chemical reactions and experiments, followed by NMR and mass spectrometer analysis.
Synthesis of compound 2-5

To a 250 mL, two-necked round bottom flask containing compound 2-4 (5.1 g, 9.43 mmol), bis(pinacolato)-diboron (4.78 g, 18.8 mmol), KOAc (3.7 g, 37.7 mmol) and PdCl2(dppf) (0.15 g, 0.184 mmol), 1,4-dioxane (180 mL) was added with stirring under N2 protection. The reaction mixture was heated to 80°C for 24 h. Solvent was removed by rotary evaporator and then the residue was diluted with water. The aqueous solution as extracted using dichloromethane. The organic layer was combined and dried over Na2SO4. The crude product was purified via column chromatography to afford a light yellow powder of 2.94 g with 53% yield. 1H NMR (400MHz, CDCl3, δ): 8.13 (d, J = 7.7 Hz, 2H), 8.04 (d, J = 16 Hz, 2H), 7.57 (m, 4H), 7.43 (m, 4H), 7.28 (m, 2H), 4.44 (q, J = 7.2 Hz, 2H), 4.19 (q, J = 7.2 Hz, 2H), 1.55 (m, J = 12 Hz, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H). 13C NMR (100MHz, CDCl3, δ): 168.3, 167.3, 141.2, 140.8, 139.8, 137.2, 136.6, 137.2, 136.4, 134.1, 134.0, 130.6, 130.0, 126.7, 126.1, 123.5, 120.5, 120.2, 109.8, 84.5, 75.0, 67.1, 61.7 (d), 25.0, 24.9, 24.6. MS (MALDI-TOF, m/z): found 589.2680 [M+H]+.

Synthesis of compound TA(TL)-Ph(3)-CBZ

Compound 2-5 (2.94 g, 4.99 mmol), palladium (II) acetate (60 mg), triphenylphosphine (0.66 g, 2.5 mmol), 4M potassium carbonate (5 mL), ethanol (40 mL) and toluene (50 mL) were added to a 250 mL two-necked round bottom flask. The reaction mixture was refluxed at 80°C with nitrogen protection for 36 h. After cooling down to room temperature, the reaction mixture was quenched with water and acidified by 6M HCl (3 mL). Thereafter, it was extracted with 3 portions of ethyl acetate, then concentrated in vacuo. A yellow sticky oil was obtained after purification via column chromatography to afford a light yellow powder of 2.94 g with 53% yield.

Synthesis of compound TA(TL)-Ph(3)-CBZ

To a 250 mL, two-necked round bottom flask containing compound 2-6 (659 mg, 0.389 mmol), 1-bromo-4-decylbenzene (3.47 g, 11.67 mmol) and anhydrous THF (40 mL) with stirring and N2 protection at -78°C, 2.5M n-BuLi (3.6 mL, 9.0 mmol) was added dropwise over 20min. The reaction solution was then concentrated to stir for 2h with the temperature lower than -70°C then warmed overnight under ambient temperature and N2 protection. The mixture was then quenched with hydrochloric acid at 0°C and extracted using three portions of ethyl acetate. The organic layers were combined, washed with brine and dried over Na2SO4. A sticky yellow oil was obtained after concentration in vacuo and then directly used in the next step. To the yellow oil obtained in the previous step, 40 mL dichloromethane was added followed by trifluoromethanesulfonic acid (0.15 M, 10 mL) in CH2Cl2/THF (1:100). The reaction mixture was continued to stir for 24 hr at room temperature with N2 protection. The solution mixture was quenched with water and its organic layer was extracted with two portions of DCM. The organic layers were combined, washed with H2O and dried over Na2SO4. The solution was then concentrated by rotary evaporator. Purification of crude product was carried out by column chromatography with and obtained yellow solid (477 mg, 0.124 mmol) with the total percentage yield (2 steps) of 31.2%. 1H NMR (400MHz, CDCl3, δ): 8.74 (m, 6H), 8.15 (d, J = 8H, 6H), 8.0-7.8 (m, 12H), 7.66 (m, 3H), 7.58 (d, J = 8 Hz, 3H), 7.43 (m, 15H), 7.30 (m, 27H), 7.22-7.03 (m, 27H), 2.59 (q, J = 8 Hz, 8H), 1.62 (d, J = 4.5Hz, 21H), 1.26 (m, 168H), 0.87 (q, J = 6.7 Hz, 36H). 13C NMR (100MHz, CDCl3, δ): 171.5, 167.8 (d), 144.6, 141.0, 140.8, 139.3, 137.4, 135.7, 133.7 (d), 132.2 (d), 130.1, 129.0 (d), 126.8, 126.1, 123.6, 109.8, 61.7 (d), 14.0. MS (MALDI-TOF, m/z): found 1693.6163 [M+H]+.

Figure 5. UV-vis absorption and fluorescence spectra of star-shaped oligomers in toluene.

The optical properties of newly synthesized compound TA(TL)-Ph(3)-CBZ were achieved by using UV-Visible and fluorescence spectroscopy. TA(TL)-Ph(3)-CBZ has good solubility in either chloroform or toluene but very insoluble in DMF unless heating, which is not suitable to characterize its linear optical properties in DMF. The linear optical properties were listed as well as the thermal property in Table-1. The UV-Visible and fluorescence spectra are shown in Fig.5 and Fig.6. As shown on the optical spectra Fig.5 and Fig.6, TA(TL)-Ph(3)-CBZ exhibited a blue shift from the others, which suggests the intramolecular charge transfer is significantly differ from the prototypes. Absorption below the 320 nm region represents a higher energy acquisition responsible for the transition from n to π* of the lone pair electron of carbazole moiety. More intensive absorption between 380 nm and 420 nm depicting the transition of π-π* of the n-conjugated bridges.

The result suggests the carbazole moiety acts differently in terms of electron inductive effect that means the N-substituted carbazole may largely weakens its electron withdrawing effect when compared with TA(TL)-Ph(3)-NPh. The observed derivation can be rationalized by the lower degree of electric polarization of the π-conjugated bridges of the π* electronic transition from n to π* of the n-conjugated cores end-capped with carbazole.

TA(TL)-Ph(3)-CBZ has a blue shift on fluorescence spectrum upon excitation in chloroform when compared with the excitation in toluene, which suggests solvatochromic effect takes place in emission spectrum conducted using chloroform.

RESULT AND DISCUSSION

Synthesis

The acceptor core was synthesized with the yield of 80% by cyclotrimerization of para-bromobenzonitrile catalyzed by trifluoromethanesulfonic acid. The compound 2-2 was efficiently synthesized by Ullmann-type condensation which possessed a high selectivity in giving the mono-substituted, even if the addition of 2 to 6 equivalent para-dibromobenzene. Hence, a borylation was carried out to give the intermediate compound 2-3 which is the precursor used in synthesizing the compound 2-4 via palladium-catalyzed Suzuki coupling. Thereafter, a borylation of compound 2-4 was carried out to give the precursor compound 2-5 in the next step. A three-fold Suzuki coupling was conducted between compound 2-5 and TAZ to afford compound 2-6 which was converted to TA(TL)-Ph(3)-CBZ via nucleophilic attack 1-bromo-4-decylbenzene and ring-closure catalyzed by trifluoromethanesulfonic acid (Scheme1).

Linear optical properties

The thermal properties of the synthesized compound TA(TL)-Ph(3)-CBZ were characterized by thermogravimetric analysis. TA(TL)-Ph(3)-CBZ exhibits similar decomposition temperature with the synthesized prototypes of MPA active oligomers N(TL)-Ph(3)-CBZ, TA(TL)-Ph(3)-NPh and (L)-Ph(3)-NPh.
Figure 6. UV-vis absorption and fluorescence spectra of star-shaped oligomers in Chloroform.

Table 1: Summary of linear optical measurements of star-shaped oligomers.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>((L)-\text{Ph}(3)-\text{NPh})</th>
<th>((N(TL)-\text{Ph}(3)-\text{NPh}))</th>
<th>((T(A(TL)-\text{Ph}(3)-\text{CBZ}))</th>
<th>((T(A(TL)-\text{Ph}(3)-\text{CBZ}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_{\text{a}}) /nm (ε)</td>
<td>405(0.77)</td>
<td>429(1.74)</td>
<td>427(1.65)</td>
<td>399(1.40)</td>
</tr>
<tr>
<td>(\lambda_{\text{b}}) /nm</td>
<td>417,443</td>
<td>443</td>
<td>461</td>
<td>430</td>
</tr>
<tr>
<td>(\lambda_{\text{c}}) /nm (ε)</td>
<td>404(0.64)</td>
<td>423(1.35)</td>
<td>426(1.54)</td>
<td>399(1.42)</td>
</tr>
<tr>
<td>(\lambda_{\text{d}}) /nm</td>
<td>421,444</td>
<td>451</td>
<td>510</td>
<td>459</td>
</tr>
<tr>
<td>(\lambda_{\text{e}}) /nm</td>
<td>403</td>
<td>427</td>
<td>427</td>
<td>Insoluble</td>
</tr>
<tr>
<td>(\lambda_{\text{f}}) /nm</td>
<td>428</td>
<td>457</td>
<td>591</td>
<td>Insoluble</td>
</tr>
<tr>
<td>(\Phi_{\text{c}})</td>
<td>0.85'</td>
<td>0.86'</td>
<td>0.90'</td>
<td>0.87'</td>
</tr>
<tr>
<td>(T_{\text{d}})/°C</td>
<td>435</td>
<td>463</td>
<td>426</td>
<td>448</td>
</tr>
</tbody>
</table>

*a average of three independent measurements using toluene, molar absorption coefficients; \((10^{4} \times \text{M}^{-1} \times \text{cm}^{-1})\). b average of three independent measurements using chloroform, molar absorption coefficients; \((10^{4} \times \text{M}^{-1} \times \text{cm}^{-1})\). c using Norharman \((\Phi_{330-390}=0.58)\) as standard. d average of two independent measurements using DMF. e determined by TGA analyer with a heating rate of 20°C/min under nitrogen.

CONCLUSION

In summary, star-shaped ladder-type ter(p-phenylene) compound composed of \(1,3,5\)-triazine core with alkylphenyl group attached \(\pi\)-conjugated arms end-capped with carbazole was synthesized and characterized for its optical and thermo properties. \(T(A(TL)-\text{Ph}(3)-\text{CBZ})\) exhibits a blue shift when compared with other compounds composed of either triazine or triphenyl core with the terminals of diphenylamine. \(T(A(TL)-\text{Ph}(3)-\text{CBZ})\) can potentially be employed in the application of blue-light emitting materials with strong emission of blue shifted light.

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REFERENCES


Non Linear Optical Properties

Two-photon excited fluorescence will be achieved as to determine the 2PA and 3PA cross-section as well as the frequency up-conversion efficiency when the related instruments are repaired.